PERMEABILITY AND SELECTIVITY STUDY OF POLYETHERSULFONE MEMBRANE FOR GAS SEPARATION

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ABSTRACT

The objective of this study is to develop and study the effect of polymer concentration and coating treatment on the membrane performance. The asymmetric polyethersulfone membranes were prepared through a dry/wet phase inversion process. The casting solution developed in this research consisted of polyethersulfone pellet, 1-methyl-2-pyrolidone (NMP) and methanol. There are three different membrane composition was prepared. The composition is 18 wt%, 23 wt% and 28 wt% of PES was used for permeability test PES membrane was divided into two categories: uncoated and coated with bromine solution. Casting process was done by using manual casting knife. Permeation test was carried out by testing CO_2 and CH_4 permeating through the membrane to check the permeability and selectivity of respective gas to CH_4. Different coating agent gave different rate of permeate while higher polymer concentration enhance the permeation rate. The PES membrane uncoated showed the higher selectivity compare to coat with bromine solution. The selectivity of CO_2/CH_4 was approximately 2.06 at 23% of PES concentration uncoated with bromine. It was believed that different concentration strongly affects the membrane performance.

ABSTRAK

Objektif kajian ini dilakukan adalah untuk membangunkan dan untuk mengkaji kesan kepekatan larutan dan kesan salutan terhadap pencapaian membran. PolyIetersulfona (PES) membran yang tidak simetri telah disediakan menggunakan teknik proses yang ringkas iaitu fasa balikan basah/kering.larutan bahan teracuan yang disediakan untuk kajian ini mengandungi PES, 1-methyl-2-pyrolidone (NMP) dan methanol.Komposisi membrane 18 wt%, 23wt% dan 28wt% digunakan untuk ujian ketelapan. Membrane PES dibahagikan kepada dua kategori , tanpa salutan dan dengan salutan bromin. Proses tebaran dilakukan menggunakan pisau tebaran manual. Ujian ketelapan telah dijalankan dengan menguji gas CO_2 dan CH_4 ke atas membran untuk melihat ketelapan dan pemilihan bagi setiap gas terhadap CH_4. Agen salutan berbeza memberikan nilai ketelapan yang berbeza manakala lebih tinggi kepekatan polimer meningkatkan kadar ketelapan. Membran PES tanpa salutan menunjukkan kadar pemilihan yang tinggi berbanding dengan membran PES dengan salutan larutan bromine. Oleh itu pemilihan bagi CO_2/CH_4 adalah 2.06 pada 23 wt% bagi kepekatan PES tanpa salutan. Maka agen salutan di percayai mempengaruhi prestasi membran dan begitu juga kepekatan polimer

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CO_2	-	Carbon Dioxide
CH_4	-	Methane
PES	-	Polyethersulfone
O_2	-	Oxygen
N_2	-	Nitrogen
H_2	-	Hydrogen
Cl	-	Chlorine
C_2	-	Carbon
ºC	-	Degree celcius
P	-	Permeability
Q	-	Flow rate
A	-	Area
ΔP	-	Pressure difference of penetrant across membrane
α	-	Selectivity
%	-	Percentage
P	-	External gas partial pressure

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CHAPTER 1

1.1 Introduction

1.1.1 Background of Study

Currently gas separation by selective permeation through polymer membrane is one of the fastest growing branches of the separation technology. Gas separation membrane systems have received a lot of attention from both industry and academia. This is because there is a belief that membrane separation processes in some application. In order to accomplish this objective, membrane materials with superior permeability and selectivity and advanced fabrication technologies to yield hollow fibers with an ultra-thin dense selective layer are the primary focuses for most membrane scientists in the last two decades.

Most of the membrane expert have been investigating and synthesizing new polymers that are able to exhibit both higher gas permeability and selectivity since the past 40 years. Presently the structure, pressure-normalized flux and selectivity of the membrane polymer have become the focus of the studies among researchers. In addition they are aiming for defect free ultra thin dense selective layer membrane material. Significant processes have been made in the membrane materials, dope preparation, fabrication technology and fundamental understanding of membrane formation

The selectivity was believed relates to the parameter such as polymer concentration used which strongly affects the membrane performance (Koros et al 2000). Selectivity of membrane can be represented by the ratio of the permeability of any two components through the membrane. This specific characteristic of a membrane were generally varies inversely with gas permeability which means to achieve a high selectivity, it requires the membrane to operate in low permeability (Scott, 1998).

Based on the previous researchers the limitation of this research was to achieve high gas permeability without a significant decrease in gas selectivity. In order to get the high selectivity membrane without reducing the permeability of membrane, low cost polymer polyethersulfone membrane was sough off. Ideally, membranes should exhibit high selectivity and high permeability. For most membranes, however, as selectivity increases, permeability decreases, and vice versa. That's the trade-off. (Hwang, 1975)

In term of material development, membrane prepare from polyethersulfone (PES) have been received special attention for gas separation due to some of them possessing surprisingly high gas selectivity for gas pair O_2/N_2 and CO_2/CH_4. Polyethersulfone also have many other desirable properties, such as spin ability, thermal and chemical stability and mechanical strength. These properties are essential to yield a membrane module with stable and predicable long-term performance (Baker, 2008).

1.2 Problem Statement

Today, oil and gas companies were required to remove or substantially reduce CO_2 levels in exhaust streams before they are vented to the atmosphere. Since CO_2 was well known as an acid gas, CO_2 should be removed before natural gas can be distribute to the pipelines. The amount of carbon dioxide should be in small amount because carbon dioxide when react with water will form carbonic acid which may corrode the pipeline. In other to meet the quality standards specified by major pipeline transmission and distribution companies one of the specifications was to ensure the pipeline free of particulate solids and liquid water. Therefore, CO_2 should be remove or the acid gases because they can lead erosion, corrosion and other damage that will not follow the standardization. (Surkov et al, 2000)

A simple process technology was highly desirable which can be applied in remote, unattended or offshore situations. In addition to competitive capital and operating cost, ease operation, quick start-up, and high on stream factors are needed. Currently amine absorption was commonly used for CO_2 separation process. Amine absorption was an effective technique to remove CO_2, however this technique complex and have high capital, operating and installation costs. Therefore new development of separating gas using membrane was developed. However the major problems confronting the use of the membrane based gas separation processes in a wide range of applications was the lack of membranes with high selectivity. Ideally, membranes should exhibit high selectivity and high permeability. For most membranes, however, as selectivity increases, permeability decreases, and vice versa. In order to get the high selectivity membrane without reducing the permeability of membrane, low cost polymer polyethersulfone membrane was sough off.

1.3 Objective of Study

To study the polymer concentration in order to find out the best formulation that gives the best performance of the membrane developed

1.4 Scope of Study

In order to meet the objective, there were some scopes which need to be focused:

i) To develop polyethersulfone polymer as a membrane for gas separation.

ii) To fabricate polymer with coating agent.

iii) To study the permeability and selectivity of different gases (CO_2, CH_4)

CHAPTER 2

LITERATURE REVIEW

2.1 History of Membrane Based Separation

Membrane based separation processes over the last three decades have proved their potential as better alternatives to traditional separation processes. Although report concerning the permeability of synthetic membranes date back to the mid 19^{th} century, membrane science and technology study started as early in 15^{th} century(Boretos,1973).

The gas separation early demonstration was using natural rubber membranes date back to the 1830's. gas separation using polymeric membranes has achieved important commercial success in some industrial processes since the first commercial scale membrane gas separation system was produced in the late 1970's.in order to extend its application and compete successfully wait traditional gas separation, processes such as cryogenic, pressure swing adsorption and absorption and researches made great attention in fabricating high separation performance in both academia an industry (Wang et al, 2002). Table 2.1 shows the milestone in the development of membrane based separation.

Table 2.1: Milestone in the development of membrane based separation

Name of inventor	**Year**	**Invention**
Abbe Nollet	1748	Wine and water separated with animal skin by reverse osmosis
J.K Mitchell	1831	First scientific observation related to gas separation
Thomas Graham	1850	Graham's law of diffusion
J.S. Chiou and D.R. Paul	1987	Prove for the two membranes as a function of CO_2 conditioning and driving pressure
Stern *et al*	1989	Development of nine types of polyimide membranes.
Suzuki *et al*	1998	Fabricated dual-layer hollow fiber membranes composed of a dense polyimide outer layer and a sponge-like inner layer made of another polyimide.
I. Cabasso	1979	Development of polyethyleneimine/polysulfone (PS) hollow fibers for RO.
Nitto Denko	1988	Develop first commercial vapor separation plants.
Li *et al*	2002	Conducted the first systematic study to investigate the effects of spinning conditions on dual-layer hollow fiber membranes and the causes of interfacial\delimitation between the two layers

A significant advance on polymeric materials for gas separation has also been made in the last 20 years (Koros et al 1988) , many high-permeability and high permselectivity materials have been discovered and synthesized. However, these high performance polymeric materials are often very expensive, while some of them are brittle.

As a result, the fabrication of integrally skinned asymmetric membranes is either no longer feasible or economically attractive because it is too costly to prepare the entire membrane from the same material.

The modern era of gas separation membrane was introduced when polymeric membrane became economically viable. H_2- recovery was the first major application of membrane gas separation technology followed by the CO_2/CH_4 separation and the production of N2 from air (Pereira,1999).

Then the membrane based gas separation has grown into a US$150 million per year business and substantial growth in the near future is likely. Several research studies (Pereira, 1999: Di Luccio, 1994: Pinnau, 1994) have focused the membrane formation in order to control the properties of the resulting membrane and optimize the applications, compared to the other developing membrane process such as gas separation and pervaporation (Souza *et al*, 1998).

2.2 Membrane Definition

Membrane is defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid; can carry a positive or negative charge or be neutral or bipolar. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 10 microns to few hundred micrometers *(*M. Takht Ravanchi *et al (2009).*

Membrane in the original word is known as "membrane" in Latin which mean as skin. Another definition of membrane can be defined as thin barrier that permits selective mass transport or a phase that acts as a barrier to prevent the mass movement, but allows or regulated passage of one or more species (Bhattacharya *et al.*, 2004).

2.3 Membrane Module

Large membrane areas are normally required in order to apply membranes on a technical scale. A module was defined as the smallest unit into which the membrane area packed. At certain flow rate and composition, a feed enters the module. Both the feed composition and flow rate inside the module change as a function of distance. This was due to the ability of membrane which able to transport one component more readily than other. There are four major types of modules normally used in membrane separation processes which are spiral wound, plate and frame, tubular and hollow fiber.

2.3.1 Spiral Wound Module

Spiral wound module consist of two layers of membrane, placed onto a permeate collector fabric. This membrane envelope is wrapped around a centrally placed permeate drain (see picture below). This causes the packing density of the membranes to be higher. The feed channel is placed at moderate height, to prevent plugging of the membrane unit. Spiral membranes are only used for nanofiltration and reverse osmosis (RO) applications (Lenntech, 2008)

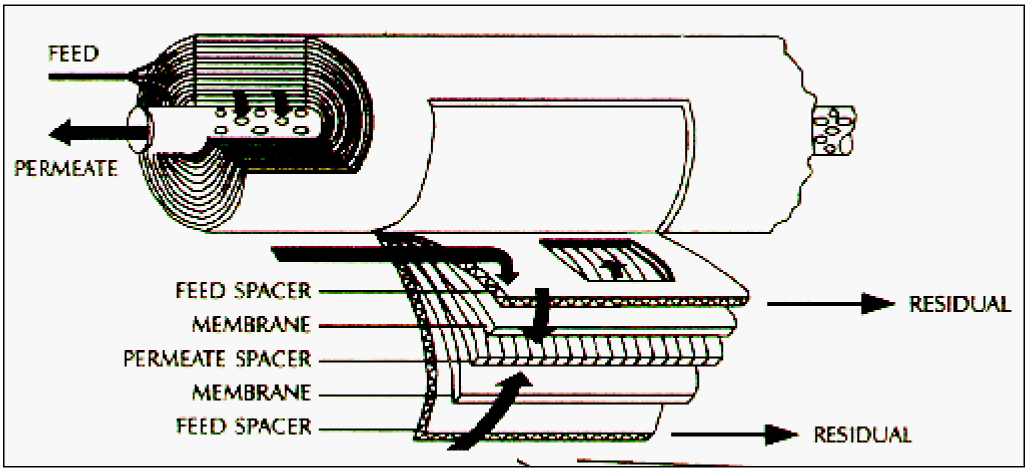

Figure 2.1: Structure of spiral wound membrane module (Lenntech, 2008)

2.3.2 Tubular Module

Tubular membranes are not self-supporting membranes. They are located on the inside of a tube, made of a special kind of material. This material is the supporting layer for the membrane. Because the location of tubular membranes is inside a tube, the flow in a tubular membrane is usually inside out. The main cause for this is that the attachment of the membrane to the supporting layer is very weak. Tubular membranes have a diameter of about 5 to 15 mm. Because of the size of the membrane surface, plugging of tubular membranes is not likely to occur. A drawback of tubular membranes is that the packing density is low, which results in high prices per module.

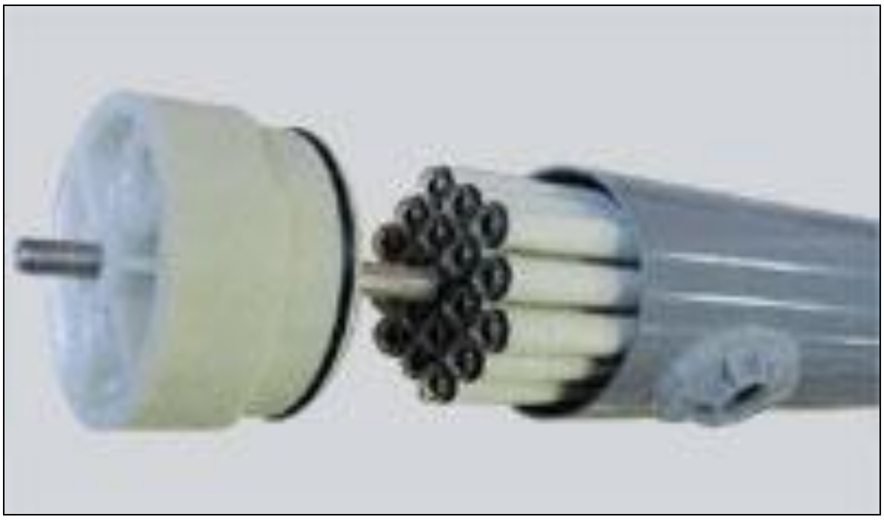

Figure 2.2: Structure of tubular module (Lenntech, 2008)

2.3.3 Hollow Fiber Module

Hollow fiber membranes are membranes with a diameter of below 0.1 µm. consequentially, the chances of plugging of a hollow fiber membrane are very high. The membranes can only be used for the treatment of water with a low suspended solid content.

The packing density of a hollow fiber membrane is very high. Hollow fiber membranes are nearly always used merely for nano filtration and reverse osmosis (RO).

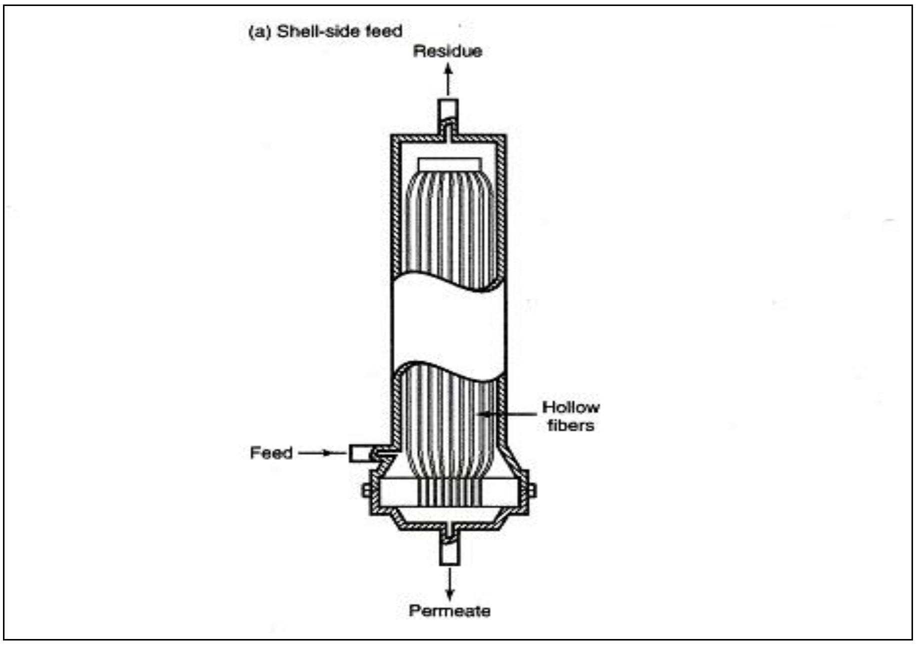

Figure 2.3: Structure of hollow fiber module (Wang *et al*., 1992)

2.3.4 Plate and Frame Module

Plate-and-frame modules were one of the earliest types of membrane system. A plate-and-frame design (Stern *et.,al,* 1965) for early Union Carbide plants to recovery helium from natural gas is shown in Figure 2.4. Membrane, feed spacers, and product spacers are layered together between two end plates. The feed mixture is forced across the surface of the membrane. A portion passes through the membrane, enters the permeate channel, and makes its way to a central permeate collection manifold.

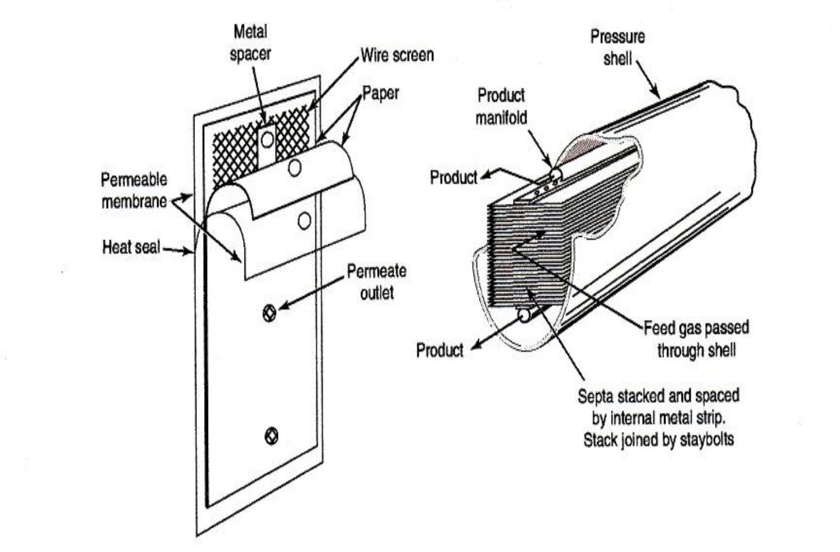

Figure 2.4: Early plate-and-frame designs developed for the separation of helium from natural gas. (Wang *et al*., 1992)

2.4 Membrane Structure

There are two types of membrane structure namely, symmetric and asymmetric. The different between these two structures were the physical and chemical properties.

2.4.1 Symmetric Membrane

A symmetric membrane was membrane that having the same chemical and physical structure throughout the hole. There are two type of symmetric membrane: porous and non-porous.

2.4.1.1 Porous Membrane

A porous membrane is a rigid, highly voided structure with randomly distributed inter-connected pores. The separation of materials by porous membranes is mainly a function of the permeate character and membrane properties like the molecular size of the membrane polymer and pore size distribution.

Porous membrane for gas separation can exhibit very high levels of flux but provide for lseparation and low selectivity (Pandey, 2001).

2.4.1.2 Non-Porous Membrane

The nonporous layer meets the requirements of the ideal membrane, that is, it is highly selective and also thin. The porous layer provides mechanical support and allows the free flow of compounds that permeate through the nonporous layer. Although asymmetric membranes are a vast improvement on homogenous membranes, they do have one drawback. Because they are composed of only one material, they are costly to make out of exotic, highly customized polymers, which often can be produced only in small amounts.

2.4.2 Asymmetric Membrane

A membrane having different chemical and physical structures in direction of thickness was called an asymmetric or anistropic membrane. This structure was characterized by a non uniform structure an active top layer or skin supported by a porous support or sub-layer. Three types of asymmetric membrane were porous, porous with top layer and composites (Scott, 1998). Figure 2.5 show the asymmetric membrane structure and Figure 2.6 show the typical type of membrane structure.

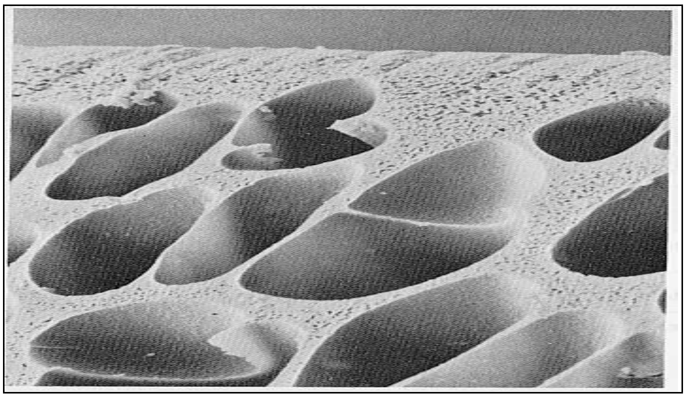

Figure 2.5: Asymmetric membrane structure

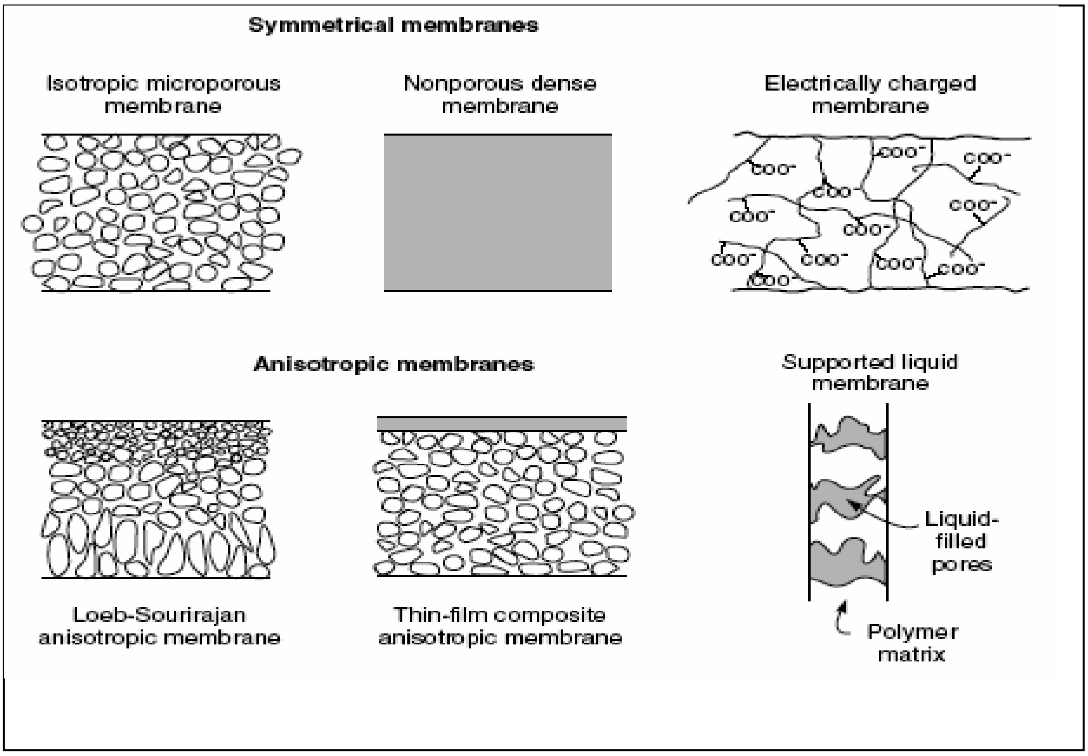

Figure 2.6: Typical types of membrane structure

2.5 Types of Membrane

2.5.1 Polymeric membranes

Generally, gas molecules transport through a polymeric membrane by a solution diffusion mechanism. Other mechanisms include a molecular sieve effect and Knudsen diffusion (Powell and Qiao, 2006).

These transport mechanisms are briefly introduced in inorganic membrane section. The terms permeability and selectivity are used to describe the performance of a gas separation membrane. There appears to be a trade-off between selectivity and permeability. Gas molecules tend to move through free volumes–the gaps between polymeric structures. Because of the movement of the polymer chains, a channel between gaps can be formed allowing gas molecules to move from one gap to another and thus gas molecules can effectively diffuse through the membrane structure. Selective transport of gases can be achieved by use of a polymer which forms channels of a certain size. Large channels will allow faster diffusion of gases through a membrane at the cost of less selectivity.

Membranes are a low cost means of separating gases when high purity is not vital. There are a number of issues associated with the capture of carbon dioxide from flue gas which limit the use of membranes. The concentration of carbon dioxide in flue gases is low, which means that large quantities of gases will need to be processed. The high temperature of flue gases will rapidly destroy a membrane, so the gases need to be cooled to below 100°C prior to membrane separation. The membranes need to be chemically resistant to the harsh chemicals contained within flue gases, or these chemicals need to be removed prior to the membrane separation.

Additionally, creating a pressure difference across the membrane will require significant amounts of power. Polymers studied in various studies include: polyacetylenes (Stern, 1994), polyaniline (Illing *et al*., 2001), poly (arylene ether)s (Xu *et al*., 2002), polyarylates (Pixton and Paul, 1995), polycarbonates (Aguilar-Vega and Paul, 1993), polyetherimides (Li and Freeman, 1997), poly (ethylene oxide) (Lin and Freeman, 2004), polyimides (Stern *et al*., 1989), poly(phenylene ether) (Aguilar-Vega and Paul, 1993), poly(pyrrolone)s (Zimmerman and Koros, 1999) and polysulfones (Aitken *et al*., 1992). Table 2.2 shows molecular structures of some commonly used polymers. The performances of some polymeric membranes are summarized in figure mainly separating post-combustion flue gas with CO2/N2 being the main components (Powell and Qiao, 2006).

Table 2.2 : Performance of polymeric membranes separating CO_2/N_2 (Powell and Qiao, 2006)

Material	**Permeance (m^3/m^2.Pa.s)**	**Selectivity**
Polyimide	7.35	43
Polydimethylphenylene oxide	2750	19
Polysulfone	450	31
Polyethersulfone	665	24.7
Poly (4 vinylpyridine /polyetherimide)	52.5	20
Polyacrylonitrite with (ethylene glycol)	91	27.9
Poly (amide-6-b-ethylene oxide)	608	61

Materials for effective separation of gases can follow one of two overall strategies: increasing the rate of diffusion of carbon dioxide through the polymeric structure and increasing the solubility of carbon dioxide in the membrane. The introduction of mixed-matrix membranes may allow superior performance which combines the advantages of polymeric and inorganic membranes materials.(Koros 1998. Figure 2.7 show examples of polymer molecular structures used for CO_2separation (Powell and Qiao, 2006).